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(54) **CONCRETE ADMIXTURE**

**BETONZUSATZMITTEL**

**AGENT DE MELANGE POUR BETON**

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(56) References cited:  
**WO-A-95/16643**

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**EP 0 846 090 B1**

## Description

[0001] The present invention relates to a concrete admixture. More specifically, it relates to a concrete admixture which is extremely effective in imparting fluidity to a hydraulic composition such as cement paste, mortar and concrete, particularly in retention of fluidity of the composition, and which hardly retards the hardening property of the composition.

[0002] So-called high performance water reducing agents have been known for use as concrete admixtures which can impart high fluidity, and examples thereof include salts of naphthalenesulfonic acid/formaldehyde condensates (naphthalene derivatives), salts of melaminesulfonic acid/formaldehyde condensates (melamine derivatives), salts of sulfanilic acid/phenol formaldehyde co-condensates (aminosulfonic acid derivatives) or salts of polycarboxylic acids (polycarboxylic acid derivatives).

[0003] Each of these admixtures has some problems, though each has excellent functions. For example, the naphthalene derivatives and the melamine derivatives are excellent in hardening characteristics, however are problematic on retention of fluidity (owing to their tendency to cause a slump loss). On the other hand the polycarboxylic acid derivatives had a problem of retarding the hardening property of the composition. Recently polycarboxylic acid concrete admixtures which can impart excellent fluidity have been developed, which makes it possible to attain excellent dispersion with a reduced amount of an admixture, and thereby the problem of retarding the hardening property is being solved. Such admixtures include water-soluble vinyl copolymers such as copolymers of polyalkylene glycol monoester monomers having unsaturated bonds with acrylic acid and/or unsaturated dicarboxylic acid monomers (see JP-A 58-74552, JP-A 62-78137, JP-A 62-119147, JP-A 3-75252 and JP-A 59-162160).

[0004] These water-soluble copolymers each exhibit an excellent dispersing effect even when used in a reduced amount, so that the retardation is improved comparatively. Further, as described in JP-A 59-162160, they are somewhat effective also on retention of dispersion. However, the copolymers cannot satisfactorily effect on retention of fluidity for a long time.

[0005] Under these circumstances, the inventors of the present invention have proposed in JP-A 7-223852 (corresponding to WO-A 95/16643) an improvement of slump loss by the use of a copolymer having a long polyoxyalkylene chain as an admixture. The technique described therein makes it possible to maintain the slump at a suitable level for a long period of time as 60 to 90 minutes.

[0006] However, it has been needed to maintain the slump for about 2 hours to cope with the delay of concrete processing due to traffic jam or troubles in construction. Therefore, the above effect of maintaining the slump for about 90 minutes is still insufficient and required to be further improved. Further, an improvement in the effect of maintaining the slump is liable to cause a problem of retarding the hardening property, so that such an improvement is also required to be attained without retarding the hardening property.

[0007] The inventors of the present invention have intensively studied on gradual supply of a dispersing agent as a means for maintaining the dispersed state of cement particles and thereby keeping the slump for a long time. Namely, the inventors of the present invention have designed the molecular structure of a dispersing agent from the viewpoint of the rate of adsorption in a strongly ionized concrete system, and have found that a vinyl copolymer comprising an oxyalkylene group and a specific monomer exhibits an extremely excellent slump-maintaining effect and that the copolymer makes it possible to maintain the slump for a time much longer than that of the prior arts without retarding the hardening property.

[0008] Namely, the present invention provides a concrete admixture comprising a copolymer essentially consisting of, as structural units, 0.1 to 50 mole % of units derived from an ethylenically unsaturated monomer (a) having 25 to 300 moles per mole of said monomer, of  $C_2 - C_3$  oxyalkylene groups and 50 to 99.9 mole % of units derived from a monomer (b) of an alkyl, alkenyl or hydroxyalkyl ester of an ethylenically unsaturated mono- or di-carboxylic acid, or 0.1 to 50 mole % of the units derived from said monomer (a), 50 to 90 mole % of the units derived from said monomer (b) and 0.1 to 50 mole % of units derived from a monomer (c) selected from an ethylenically unsaturated monocarboxylic acid, a salt thereof, an ethylenically unsaturated dicarboxylic acid, an anhydride thereof and a salt thereof.

[0009] The present invention provides a method for dispersing a cement mixture with said copolymer.

[0010] The present invention provides a concrete composition comprising cement, aggregates and the copolymer.

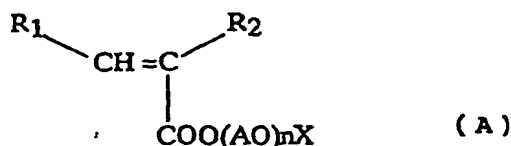
[0011] The present invention provides use of the copolymer to mix and disperse a cement mixture.

[0012] The present invention also provides an embodiment, in which the copolymer comprises 10 to 30 mole % of the units (a), 50 to 70 mole % of the units (b) and 10 to 30 mole % of the units (c), wherein the units (c) are derived from a monomer (c) selected from an ethylenically unsaturated monocarboxylic acid, a salt thereof, an ethylenically unsaturated dicarboxylic acid, an anhydride thereof and a salt thereof. The dispersion can be maintained over a period of 120 minutes or longer. Retardation of the hardening property can be thereby reduced.

[0013] When the concrete admixture is used for concrete, an extremely excellent slump-maintaining effect can be attained, the reason for which is considered to be that the dispersing agent is gradually taken into hydrates of cement to prevent the fluidity from lowering. In other words, it is assumed that oxyalkylene groups and the units derived from the specific monomer in the copolymers may influence the rate of adsorption to cement.

[0014] The concrete admixture comprises a copolymer comprising, as structural units, units derived from an ethylenically unsaturated monomer (a) having 25 to 300 moles per mole of said monomer of C<sub>2</sub> - C<sub>3</sub> oxyalkylene groups and units derived from a monomer (b) of an alkyl, alkenyl or hydroxyalkyl ester of an ethylenically unsaturated mono- or di-carboxylic acid. Therefore, carboxyl groups which serves as an adsorbing group is gradually increased through hydrolysis of ester with an alkali to result in supplying a freshly formed dispersant, which may be the reason why the fluidity is not lowered but maintained for a long period of time. When the copolymer has lengthened side chains by an increase in the mole number of oxyalkylene groups added, it exhibits an enhanced dispersing effect due to steric repulsion and therefore can impart fluidity even when a reduced amount is used. Therefore, the surface hydration of cement is little hindered to result in a slight retardation of the hardening property. However, the present invention is not limited by these assumptions.

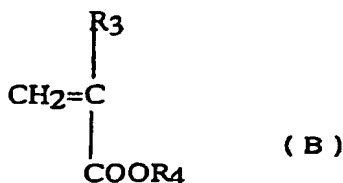
[0015] In the copolymer the ethylenically unsaturated monomer (a) having 25 to 300 moles per mole of said monomer of C<sub>2</sub> - C<sub>3</sub> oxyalkylene groups includes (meth)acrylic esters of methoxypolyalkylene glycols; polyalkylene glycol monoallyl ethers; and adducts of dicarboxylic acids such as maleic anhydride, itaconic anhydride, citraconic anhydride, maleic acid, itaconic acid and citraconic acid, acrylamide and acrylalkylamide with C<sub>2</sub>-C<sub>3</sub> oxyalkylene groups. Preferred examples of the monomer (a) include those represented by the following general formula (A):



wherein R<sub>1</sub> and R<sub>2</sub> are each hydrogen atom or methyl, AO is a C<sub>2</sub>-C<sub>3</sub> oxyalkylene group, n is a number of 25 to 300 and X is hydrogen atom or a C<sub>1</sub>-C<sub>3</sub> alkyl group.

[0016] Specific examples of the monomer (a) represented by the above formula (A) include acrylic and methacrylic esters of polyalkylene glycols blocked with an alkyl group at one end such as methoxypolyethylene glycol, methoxypolyethylenepolypropylene glycol, ethoxypolyethylene glycol, ethoxypolyethylene-polypropylene glycol, propoxypolyethylene glycol and propoxypolyethylenepolypropylene glycol; and adducts of acrylic and methacrylic acids with ethylene oxide and propylene oxide. The molar addition number of the oxyalkylene group is 25 to 300. When both ethylene oxide and propylene oxide are used, the copolymer may take any form of random addition, block addition and alternating addition. It is preferable from the viewpoint of not causing any retardation of the hardening of concrete that the number of the oxyalkylene group is 50 or above, particularly 110 or above. When the number exceeds 300, not only the polymerizability of the monomer will be poor but also the resulting copolymer will be poor in the dispersing effect.

[0017] Preferable examples of alkyl, alkenyl or hydroxyalkyl ester of an ethylenically unsaturated mono- or di-carboxylic acid to be used as the monomer (b) include unsaturated monocarboxylate ester represented by, e.g., the following general formula (B):



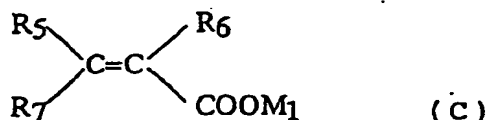
wherein R<sub>3</sub> is hydrogen atom or methyl and R<sub>4</sub> is a C<sub>1</sub>-C<sub>18</sub> alkyl or alkenyl group or a C<sub>2</sub>-C<sub>6</sub> hydroxyalkyl group.

[0018] Specific examples of the monomer (b) include C<sub>1</sub>-C<sub>18</sub> linear and branched alkyl (meth)acrylates; C<sub>1</sub>-C<sub>18</sub> linear and branched alkenyl (meth)acrylates; C<sub>2</sub>-C<sub>6</sub> hydroxyalkyl (meth)acrylates; di(C<sub>1</sub>-C<sub>18</sub> linear and branched alkyl) esters of maleic acid, fumaric acid, itaconic acid and citraconic acid; and di(C<sub>1</sub>-C<sub>18</sub> linear and branched alkenyl) esters of maleic acid, fumaric acid, itaconic acid and citraconic acid. It is particularly preferable in the solubility of the copolymer in water that R<sub>4</sub> in the above general formula (B) be one having 1 to 4 carbon atoms, though R<sub>4</sub> is not particularly limited in the form but may be any of linear and branched ones.

[0019] The copolymer is excellent in the effect of maintaining the slump, preferably when the proportions of the units (a) and (b) are 0.1 to 50 mole % and 50 to 99.9 mole % respectively. In particular, when the proportions of the monomers

(a) and (b) are 1 to 40 mole % and 60 to 99 mole % respectively, the resulting copolymer exhibits an excellent effect of low fluidity loss and is extremely excellent in the retention of slump. When the proportions of the monomers are outside the above ranges, the copolymer shows poor retention of slump.

[0020] The copolymer may further contain units derived from a monomer (c) as structural units. The monomer (c) is an ethylenically unsaturated monocarboxylic acid or a salt thereof, or an ethylenically unsaturated dicarboxylic acid or an anhydride or salt thereof, and can be represented by, e.g., the following general formula (C):



wherein  $M_1$  is hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, an alkylammonium or a substituted alkylammonium group;  $R_5$ ,  $R_6$  and  $R_7$  are each hydrogen atom, methyl or  $(\text{CH}_2)_{m_2}\text{COOM}_2$ ;  $M_2$  has the same definition as  $M_1$ ;  $m_2$  is 0 or 1.

[0021] Specific examples of the monomer (c) include monocarboxylic acid monomers such as acrylic acid, methacrylic acid and crotonic acid and salts thereof with alkali metals, ammonium, amines and substituted amines; and unsaturated dicarboxylic acid monomers such as maleic acid, itaconic acid, citraconic acid and fumaric acid and salts thereof with alkali metals, alkaline earth metals, ammonium, amines and substituted amines. Further, the copolymer may contain other monomer such as acrylamide, vinyl acetate, styrene and vinyl chloride.

[0022] In the case wherein the copolymer contains the monomer unit (c), the copolymer is excellent in the effect of maintaining the slump, when the proportions of the units (a), (b) and (c) are 0.1 to 50 mole %, 50 to 90 mole % and 0.1 to 50 mole % respectively. In particular, when the proportions of the units (a), (b) and (c) are 5 to 40 mole %, 50 to 90 mole and 5 to 40 mole %, the resulting copolymer exhibits almost no fluidity loss and shows excellent balance between initial dispersibility and retention of fluidity to permit a reduction in the amount of the admixture used.

[0023] The copolymer can be prepared by known processes, e.g. solution polymerization described in JP-A 62-119147 and JP-A 62-78137. That is, the copolymer can be prepared by polymerising the monomers (a) and (b), or the monomers (a), (b) and (c) in a suitable solvent at the above-described reacting ratio.

[0024] The solvent to be used in the solution polymerization includes water, methyl alcohol, ethyl alcohol, isopropyl alcohol, benzene, toluene, xylene, cyclohexane, n-hexane, ethyl acetate, acetone or methyl ethyl ketone. It is preferable from the viewpoints of handleability and reaction equipment to use water, methyl alcohol, ethyl alcohol and isopropyl alcohol.

[0025] Examples of the polymerization initiator usable in an aqueous medium include ammonium and alkali metal salts of persulfuric acid; hydrogen peroxide; and water-soluble azo compounds such as 2,2'-azobis(2-amidinopropane) dihydrochloride and 2,2'-azobis(2-methylpropionamide) dihydrate. Examples of the polymerization initiator usable in conducting the solution polymerization in a non-aqueous medium include peroxides such as benzoyl peroxide and lauroyl peroxide; and aliphatic azo compounds such as azobisisobutyronitrile.

[0026] A polymerization accelerator such as sodium hydrogensulfite and amine compounds may be used simultaneously with the polymerization initiator. Further, a chain transfer agent such as 2-mercaptoethanol, mercaptoacetic acid, 1-mercaptoglycerin, mercaptosuccinic acid or alkylmercaptan may be simultaneously used for the purpose of controlling the molecular weight.

[0027] It is preferable that the copolymer according to the present invention have a weight-average molecular weight of 8,000 to 1,000,000, still preferably 10,000 to 300,000 (in terms of polyethylene glycol as determined by gel permeation chromatography). When the molecular weight is too large, the copolymer will be poor in the dispersing property, while when it is too small, the copolymer will be poor in the property of maintaining the slump.

[0028] The copolymer may further comprises other comonomers, as far as the effects of the present invention are not adversely affected. Examples of such comonomers include acrylonitrile, methallylsulfonic acid, acrylamide, methacrylamide, styrene and styrenesulfonic acid.

[0029] It is preferable that the amount of the concrete admixture added to concrete be 0.02 to 1.0% by weight, still preferably 0.05 to 0.5% by weight based on cement in terms of solid matter.

[0030] The concrete admixture may further contain the above-described high performance water reducing agent.

[0031] Examples of the high performance water reducing agent include naphthalene derivatives such as Mighty 150 (a product of Kao Corporation), melamine derivatives such as Mighty 150V-2 (a product of Kao Corporation), amino-sulfonic acid derivatives such as Paric FP (a product of Fujisawa Chemicals), and polycarboxylic acid derivatives such as Mighty 2000WHZ (a product of Kao Corporation). Among these known high performance water reducing agents, it is particularly preferable to use a copolymer described in JP-A 7-223852 (corresponding to WO-A 95/16643) which is

prepared by copolymerizing a polyalkylene glycol monoester monomer, wherein the polyalkylene glycol moiety is composed of 110 to 300 moles of oxyalkylene groups having 2 to 3 carbon atoms, with an acrylic acid monomer, because the copolymer is excellent in maintaining the fluidity showing little retardation of the hardening property.

[0032] It is preferable from the viewpoint of maintaining the fluidity that the weight ratio of the concrete admixture of the present invention to the high performance water reducing agent lies between 1 : 99 and 99 : 1 (with the proviso that the sum total is 100% by weight), still preferably between 10 : 90 and 90 : 10.

[0033] The concrete admixture of the present invention may be used in combination with other known additives. Examples of such additives include an air entraining (AE) agent, an AE water-reducing agent, a plasticizer, a retarder, an early-strength enhancer, an accelerator, a foaming agent, a blowing agent, an antifoaming agent, a thickener, a waterproofing agent, a defoaming agent, quartz sand, blast furnace slag, fly ash, silica fume and so on.

[0034] The concrete admixture of the present invention can be added to a composition containing a hydraulic cement. Examples of the composition include e.g. cement pastes, mortars and concretes.

[0035] The present invention will now be described specifically by referring to the following Examples.

[0036] In the Examples, all percentages are by weight.

[0037] The weight-average molecular weights of copolymers given in the Examples are those in terms of polyethylene glycol as determined by gel permeation chromatography.

[0038] The compounds used in the following Examples as the monomer (a) will now be listed together with their symbols, wherein EO and PO refer to ethylene oxide and propylene oxide respectively; and molar addition numbers are given in terms of average ones.

A-1: methoxypolyethylene glycol methacrylate (The number of EO added: 130)

A-2: methoxypolyethylene glycol methacrylate (The number of EO added: 185)

A-3: methoxypolyethylene glycol acrylate (The number of EO added: 280)

A-4: methoxypolypropylenepolyethylene glycol(random adduct) methacrylate (The number of EO added: 125, number of PO added: 15)

A-5: adduct of maleic acid with EO (The number of EO added: 120)

A-6: adduct of allyl alcohol with EO (The number of EO added: 120)

A-7: adduct of acrylamide with EO (The number of EO added: 118)

A-8: methoxypolyethylene glycol methacrylate (The number of EO added: 28)

A-9: methoxypolyethylene glycol methacrylate (The number of EO added: 90)

A-10 (Comp.): methoxypolyethylene glycol methacrylate (The number of EO added: 350)

A-11 (Comp.): methoxypolyethylene glycol methacrylate (The number of EO added: 13)

[0039] Production Examples for the copolymers will now be described.

#### Production Example 1 (admixture C-1)

[0040] Water (26 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.05 mol of monomer A-1 and 0.95 mol of methyl acrylate, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.1 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.2 mol) was dropped into the resulting mixture in 30 minutes and the mixture thus obtained was aged at that temperature (95°C) for 2 hours. Thus, a copolymer having a molecular weight of 20,000 was obtained.

#### Production Example 2 (admixture C-2)

[0041] Water (70 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.1 mol of monomer A-2, 0.3 mol of methyl acrylate and 0.1 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.1 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.2 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.2 mol) was dropped into the resulting mixture in 30 minutes and the mixture thus obtained was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.07 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 56,000 was obtained.

## Production Example 3 (admixture C-3)

[0042] Water (209 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-3, 0.6 mol of ethyl acrylate and 0.2 mol of acrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.1 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.2 mol) was dropped into the resulting mixture in 30 minutes and the mixture thus obtained was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 134,000 was obtained.

## Production Example 4 (admixture C-4)

[0043] Water (58 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.1 mol of monomer A-4, 0.7 mol of methyl methacrylate and 0.2 mol of acrylic acid, a 10% aqueous solution of 2,2'-azobis (2-amidinopropane) dihydrochloride (0.02 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. After the completion of the dropping, the resulting mixture was aged at that temperature (75 °C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.15 mol) was dropped into the resulting mixture in 30 minutes and the mixture thus obtained was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 68,000 was obtained.

## Production Example 5 (admixture C-5)

[0044] Water (101 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-1, 0.6 mol of isobutyl acrylate and 0.2 mol of acrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.04 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes and the mixture thus obtained was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 112,000 was obtained.

## Production Example 6 (admixture C-6)

[0045] Water (56 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.25 mol of monomer A-1, 0.55 mol of ethyl acrylate and 0.2 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of mercaptosuccinic acid (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 86,000 was obtained.

## Production Example 7 (admixture C-7)

[0046] Water (56 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.25 mol of monomer A-5, 0.55 mol of methyl acrylate and 0.2 mol of monosodium maleate, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of mercaptosuccinic acid (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour. After the completion of the aging, 48% sodium hydroxide (0.07 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 34,000 was obtained.

## Production Example 8 (admixture C-8)

[0047] Water (50 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.25 mol of monomer A-6, 0.55 mol of methyl acrylate and 0.2 mol of monosodium maleate, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of mercaptosuccinic acid (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour. After the completion of the aging, 48% sodium hydroxide (0.07 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 31,000 was obtained.

## Production Example 9 (admixture C-9)

[0048] Water (50 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.25 mol of monomer A-7, 0.55 mol of methyl acrylate and 0.2 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of mercaptosuccinic acid (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 53,000 was obtained.

## Production Example 10 (admixture C-10)

[0049] Water (30 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.20 mol of monomer A-8, 0.60 mol of ethyl acrylate and 0.2 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0 - 15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 36,000 was obtained.

## Production Example 11 (admixture C-11)

[0050] Water (50 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.15 mol of monomer A-9, 0.75 mol of diethyl maleate and 0.1 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.08 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.10 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.07 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 54,000 was obtained.

## Production Example 12 (admixture C-12)

[0051] Water (50 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.40 mol of monomer A-8 and 0.60 mol of methyl methacrylate, a 20% aqueous solution of ammonium persulfate (0.10 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.06 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. Thus, a copolymer having a molecular weight of 83,000 was obtained.

## Production Example 13 (admixture C-13)

[0052] Water (45 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.1 mol of monomer A-1, 0.7 mol of methyl acrylate and 0.2 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of mercaptosuccinic acid (0.08 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour. After the completion of the aging, 48% sodium hydroxide (0.15 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 57,000 was obtained.

## Production Example 14 (admixture C-14)

[0053] Water (22 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-8 and 0.8 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.02 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.05 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75 °C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.6 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 23, 000 was obtained.

## Production Example 15 (admixture C-15)

[0054] Water (70 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-2 and 0.8 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.05 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.1 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.02 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.2 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.6 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 78,000 was obtained.

## Production Example 16 (admixture C-16)

[0055] Water (135 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75°C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-10, 0.7 mol of methyl acrylate and 0.1 mol of methacrylic acid, a 20% aqueous solution of ammonium persulfate (0.03 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.05 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. After the completion of the aging, 48% sodium hydroxide (0.07 mol) was added to the mixture. Thus, a copolymer having a molecular weight of 145,000 was obtained.

## Production Example 17 (admixture C-17)

[0056] Water (50 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75 °C in a nitrogen atmosphere. A solution comprising 0.65 mol of monomer A-8 and 0.35 mol of methyl methacrylate, a 20% aqueous solution of ammonium persulfate (0.1 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.10 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. Thus, a copolymer having a molecular weight of 265,000 was obtained.



## Production Example 18 (admixture C-18)

[0057] Water (30 mol) was charged into a reactor equipped with a stirrer, and the resulting system was purged with nitrogen under stirring, followed by heating to 75 °C in a nitrogen atmosphere. A solution comprising 0.2 mol of monomer A-11 and 0.8 mol of methyl acrylate, a 20% aqueous solution of ammonium persulfate (0.1 mol) and a 20% aqueous solution of 2-mercaptoethanol (0.06 mol) were separately and simultaneously dropped into the reactor in 2 hours. Then, a 20% aqueous solution of ammonium persulfate (0.01 mol) was dropped into the reactor in 30 minutes. The resulting mixture was aged at that temperature (75°C) for one hour and thereafter heated to 95°C. 35% hydrogen peroxide (0.1 mol) was dropped into the resulting mixture in 30 minutes, and the obtained mixture was aged at that temperature (95°C) for 2 hours. Thus, a copolymer having a molecular weight of 56,000 was obtained.

[0058] Comparative admixtures other than the comparative copolymers were also used in the Examples. The comparative admixtures will now be described together with their symbols.

NS: an admixture comprising salt of naphthalenesulfonic acid-formaldehyde condensate (Mighty 150, a product of Kao Corporation), and

MS: an admixture comprising salt of melamine-sulfonic acid-formaldehyde condensate (Mighty 150V-2, a product of Kao Corporation).

[0059] Concrete admixtures according to the present invention and comparative ones were evaluated by the following method.

<Evaluation as concrete admixture>

[0060] Materials for concrete were prepared according to the conditions specified in Table 1.

Table 1

W/C (%)	s/a (%)	Unit amt. (kg/m <sup>3</sup> )			
		C	W	S	G
57	48	300	170	867	951
Materials used					
W : tap water					
C : normal Portland cement, a product of Onoda Cement Co. Ltd.					
(specific gravity: 3.16)					
S : river sand from the Kino river					
(specific gravity: 2.60)					
G : crushed stone from Takarazuka					
(specific gravity: 2.63)					
s/a: sand/(sand + gravel) (volume ratio)					

[0061] The materials specified in Table 1 and each admixture were mixed in a tilting mixer at 25 rpm for 3 minutes to prepare a concrete. The concretes thus prepared were examined for fluidity (slump value) according the method stipulated in JIS-A1101. Then, the concretes were each further mixed at 4 rpm to determine the slump value (cm) over the period of 120 minutes. The setting time of each concrete was determined by the method stipulated in JIS-A6204 attachment 1. The initial slump of each concrete was adjusted to 20±1 cm by regulating the amount of the admixture to be added. The results are given in Table 2.

Table 2

Divi- sion	Symbol of admixture	Amt. of adding "l" (%)	Slump value (cm)					Setting time (h-min)	
			just after	after 30 min.	after 60 min.	after 90 min.	after 120 min.	initial setting	final setting
Invention product	C-1	0.27	19.0	21.2	22.0	22.5	22.5	4-52	6-31
	C-2	0.23	20.0	20.3	20.5	20.0	18.0	4-33	6-15
	C-3	0.18	19.5	20.0	19.5	18.0	17.5	4-36	6-20
	C-4	0.18	20.4	19.5	19.0	18.5	17.3	4-39	6-28
	C-5	0.20	19.5	19.5	18.5	18.0	17.2	4-48	6-55
	C-6	0.25	20.8	20.3	19.5	19.2	18.5	4-55	6-32
	C-7	0.29	20.0	19.5	19.0	18.5	15.5	5-13	6-58
	C-8	0.28	20.5	20.0	19.5	19.0	16.0	5-08	6-41
	C-9	0.30	20.5	20.0	19.0	19.0	15.5	5-19	6-57
	C-10	0.26	19.8	19.5	18.2	17.0	15.2	6-02	8-13
	C-11	0.32	20.2	19.9	19.0	17.3	15.8	5-58	7-49
	C-12	0.28	19.2	19.5	19.3	18.8	17.6	6-38	8-23
	C-13	0.25	20.6	20.5	20.0	19.5	19.2	4-52	6-27
	C-1/C-15 <sup>3</sup>	0.22	20.5	20.6	20.5	20.3	20.0	4-18	6-02
	C-14	0.23	20.7	18.0	12.5	10.5	7.0	7-20	8-58
	C-15	0.20	19.5	20.0	19.5	17.5	10.5	4-22	6-10
	C-16	0.45	20.0	16.5	13.0	11.0	10.0	4-44	6-15
	C-17	0.38	19.2	17.5	16.3	12.0	8.0	7-06	9-26
	C-18	0.4	19.5	16.5	13.5	10.0	9.5	7-25	9-00
Comp. product	NS	0.55	20.3	10.5	8.5	5.0	4.5	7-36	9-50
	MS	0.60	20.5	12.8	7.0	5.5	4.0	7-48	9-36

\*1: weight % in terms of solid matter based on the weight of cement

\*2: blend of invention C-1 with comparative C-15 (weight ratio: 50 / 50 (%))

[0062] As apparent from the results given in Table 2, the admixtures of the present invention can maintain the slump value observed just after the preparation for a lengthened time and little retard the hardening property.

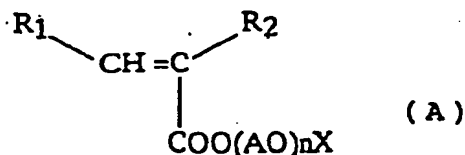
[0063] Further, the admixtures of the present invention make it possible to maintain the slump value for two or more hours, while the slump can be maintained only for at most 90 minutes when the polycarboxylic acid admixture of the comparative products are used.

[0064] Accordingly, a cement composition containing a concrete admixture of the present invention shows low level of slump loss for a long time, which facilitates the quality control of concrete even in the case wherein concrete is produced and placed under such conditions that the slump is more difficult to maintain, for example, high temperature in summer or low water/cement ratio or even in the case wherein the processing of concrete is delayed by some troubles.

[0065] C-4, C-5, C-6 and C-13 are in particular preferred.

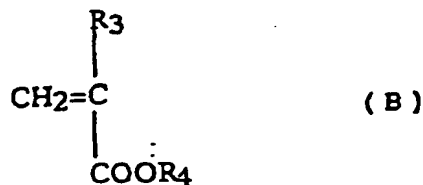
#### Claims

1. Concrete admixture comprising a copolymer essentially consisting of, as structural units, 0.1 to 50 mole % of units derived from an ethylenically unsaturated monomer (a) having per one mole thereof 25 to 300 moles of  $C_2 - C_3$  oxyalkylene groups and 50 to 99.9 mole % of units derived from a monomer (b) of an alkyl, alkenyl or hydroxyalkyl ester of an ethylenically unsaturated mono- or di-carboxylic acid, or 0.1 to 50 mole % of the units derived from said monomer (a), 50 to 90 mole % of the units derived from said monomer (b) and 0.1 to 50 mole % of units derived from a monomer (c) selected from an ethylenically unsaturated monocarboxylic acid, a salt thereof, an ethylenically unsaturated dicarboxylic acid, and anhydride thereof and a salt thereof.
2. The admixture as claimed in claim 1, in which the monomer (a) is selected from an ester product of methoxypolyalkylene glycol having per one mole 25 to 300 moles of  $C_2 - C_3$  oxyalkylene groups with acrylic acid or methacrylic acid, monoalkyl ether of polyalkylene glycol having per one mole 25 to 300 moles of  $C_2 - C_3$  oxyalkylene groups and maleic anhydride, itaconic anhydride, citraconic anhydride, maleic acid, itaconic acid, citraconic acid, acrylic amide and an acrylalkyl amide, each having per one mole 25 to 300 moles of added  $C_2 - C_3$  oxyalkylene groups.
3. The admixture as claimed in claim 1 or 2, in which the monomer (a) is defined by the formula (A):



wherein  $R_1$  and  $R_2$  are each hydrogen atom or methyl, AO is a  $C_2 - C_3$  oxyalkylene group, n is a number of 25 to 300 and X is hydrogen atom or a  $C_1 - C_3$  alkyl group.

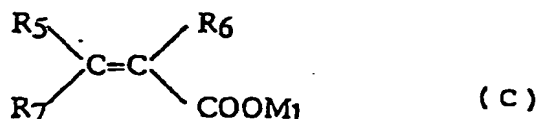
4. The admixture as claimed in claim 3, in which n is a number of 110 to 300.
5. The admixture as claimed in any one of the claims 1 to 4, in which the monomer (b) is an unsaturated monocarboxylate ester having the formula (B):



wherein  $R_3$  is hydrogen atom or methyl and  $R_4$  is a  $C_1 - C_{18}$  alkyl or alkenyl group or a  $C_2 - C_6$  hydroxyalkyl

group.

6. The admixture as claimed in any one of the claims 1 to 5 in which the monomer (b) is selected from a maleic diester; a fumaric diester, an itaconic diester and a citraconic diester, each diester being with a  $C_1-C_{18}$ , straight or branched, alkyl or alkenyl group.
7. The admixture as claimed in any one of the claims 1 to 6 which the monomer(c) is defined by the formula (c):



wherein  $M_1$  is hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, an alkylammonium or a substituted alkylammonium group;  $R_5$ ,  $R_6$  and  $R_7$  are each hydrogen atom, methyl or  $(CH_2)_{m_2}COOM_2$ ;  $M_2$  has the same definition as  $M_1$ ;  $m_2$  is 0 or 1.

8. The admixture as claimed in any one of the claims 1 to 7, in which the copolymer has a weight average molecular weight of 8,000 to 1,000,000.
9. The admixture as claimed in any one of the claims 1 to 8, in which the copolymer comprises 5 to 40 mole % of the units (a), 50 to 90 mole % of the units (b) and 5 to 40 mole % of the units (c).
10. The admixture as claimed in any one of the claims 1 to 9, in which the copolymer comprises 10 to 30 mole % of the units (a), 50 to 70 mole % of the units (b) and 10 to 30 mole % of the units (c).
11. A concrete admixture composition comprising the copolymer as defined in any one of the claims 1 to 10 and at least one high performance water reducing agent selected from the group consisting of naphthalene derivatives, melamine derivatives, aminosulfonic acid derivatives and polycarboxylic acid derivatives.
12. The composition as claimed in claim 11, in which a mixing ratio of the copolymer to the high performance water reducing agent ranges between 10 : 90 and 90 : 10.
13. A method for dispersing a cement mixture with the copolymer as defined in any one of the claims 1 to 10.
14. A concrete composition comprising cement, aggregates and the copolymer as defined in any one of the claims 1 to 10.
15. The cement composition as claimed in claim 14, which comprises 0.02 to 1.0 percent by weight based on the cement, in terms of solid matter, of the copolymer.
16. Use of the copolymer as defined in any one of the claims 1 to 10 to mix and disperse a cement mixture.
17. A process of producing the copolymer as defined in any one of the claims 1 to 10 by polymerising the monomers (a) and (b) or the monomers (a), (b) and (c) in a suitable solvent at a reaction ratio of 0.1 to 50 mole % of (a) and 50 to 99.9 mole % of (b) or at a reaction ratio of 0.1 to 50 mole % of (a), 50 to 90 mole % of (b) and 0.1 to 50 mole % of (c).

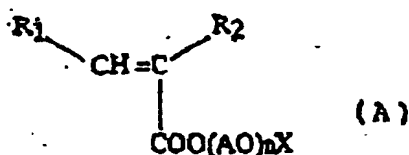
#### Revendications

1. Adjuvant pour béton comprenant un copolymère constitué essentiellement de, comme unités structurales, 0,1 à 50% en moles d'unités dérivées d'un monomère à insaturation éthylénique (a) ayant pour une mole de celui-ci 25 à 300 moles de groupes oxyalkylène en  $C_2$  à  $C_3$  et 50 à 99,9 % en moles d'unités dérivées d'un monomère (b) d'un ester d'alkyle, d'alcényle ou d'hydroxyalkyle d'un acide mono- ou di-carboxylique à insaturation éthylénique,

ou 0,1 à 50 % en moles des unités dérivées dudit monomère (a), 50 à 90 % en moles des unités dérivées dudit monomère (b) et 0,1 à 50% en moles d'unités dérivées d'un monomère (c) choisi parmi un acide monocarboxylique à insaturation éthylénique, un sel de celui-ci, un acide dicarboxylique à insaturation éthylénique, et un anhydride et un sel de celui-ci.

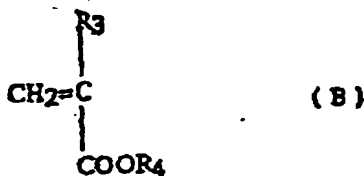
2. Adjuvant selon la revendication 1, dans lequel le monomère (a) est choisi parmi un produit d'ester de méthoxypolyalkylèneglycol ayant pour une mole 25 à 300 moles de groupes oxyalkylène en C<sub>2</sub> à C<sub>3</sub> avec un acide acrylique ou un acide méthacrylique, un monoallyl éther de polyalkylèneglycol ayant pour une mole 25 à 300 moles de groupes oxyalkylène en C<sub>2</sub> à C<sub>3</sub> et l'anhydride maléique, l'anhydride itaconique, l'anhydride citraconique, l'acide maléique, l'acide itaconique, l'acide citraconique, un amide acrylique et un alkyl amide acrylique, chacun ayant pour une mole 25 à 300 moles de groupes oxyalkylène en C<sub>2</sub> à C<sub>3</sub> ajoutés.

3. Adjuvant selon la revendication 1 ou 2, dans lequel le monomère (a) est défini par la formule (A) :



dans laquelle R<sub>1</sub> et R<sub>2</sub> sont chacun un atome d'hydrogène ou un méthyle, AO est un groupe oxyalkylène en C<sub>2</sub> à C<sub>3</sub>, n est un nombre de 25 à 300 et X est un atome d'hydrogène ou un groupe alkyle en C<sub>1</sub> à C<sub>3</sub>.

4. Adjuvant selon la revendication 3, dans lequel n est un nombre de 110 à 300.
5. Adjuvant selon l'une quelconque des revendications 1 à 4, dans lequel le monomère (b) est un ester de monocarboxylate insaturé ayant la formule (B) :



dans laquelle R<sub>3</sub> est un atome d'hydrogène ou un méthyle et R<sub>4</sub> est un groupe alkyle ou alcényle en C<sub>1</sub> à C<sub>18</sub> ou un groupe hydroxyalkyle en C<sub>2</sub> à C<sub>6</sub>.

6. Adjuvant selon l'une quelconque des revendications 1 à 5, dans lequel le monomère (b) est choisi parmi un diester maléique, un diester fumarique, un diester itaconique et un diester citraconique, chaque diester étant avec un groupe alkyle ou alcényle, en C<sub>1</sub> à C<sub>18</sub>, linéaire ou ramifié.
7. Adjuvant selon l'une quelconque des revendications 1 à 6, dans lequel le monomère (c) est défini par la formule (C) :

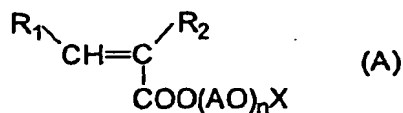


dans laquelle  $M_1$  est un atome d'hydrogène, un métal alcalin, un métal alcalino-terreux, un ammonium, un alkylammonium ou un groupe alkylammonium substitué;  $R_5$ ,  $R_6$  et  $R_7$  sont chacun un atome d'hydrogène, un méthyle ou  $(CH_2)_{m_2}COOM_2$ ;  $M_2$  a la même définition que  $M_1$ ;  $m_2$  vaut 0 ou 1.

- 5 8. Adjuvant selon l'une quelconque des revendications 1 à 7, dans lequel le copolymère a une masse moléculaire moyenne en poids de 8000 à 1000000.
9. Adjuvant selon l'une quelconque des revendications 1 à 8, dans lequel le copolymère comprend 5 à 40 % en moles des unités (a), 50 à 90 % en moles des unités (b), et 5 à 40 % en moles des unités (c).
- 10 10. Adjuvant selon l'une quelconque des revendications 1 à 9, dans lequel le copolymère comprend 10 à 30 % en moles des unités (a), 50 à 70 % en moles des unités (b), et 10 à 30 % en moles des unités (c).
- 15 11. Composition d'adjuvant pour béton comprenant le copolymère tel que défini selon l'une quelconque des revendications 1 à 10, et au moins un agent réducteur d'eau de haute performance choisi dans le groupe comprenant les dérivés du naphthalène, les dérivés de la mélamine, les dérivés acides aminosulfoniques et les dérivés acides polycarboxyliques.
- 20 12. Composition selon la revendication 11, dans laquelle un rapport de mélange du copolymère à l'agent réducteur d'eau de haute performance se situe entre 10:90 et 90:10.
13. Procédé de dispersion d'un mélange de ciment avec le copolymère selon l'une quelconque des revendications 1 à 10.
- 25 14. Composition de béton comprenant du ciment, des agrégats et le copolymère tel que défini selon l'une quelconque des revendications 1 à 10.
15. Composition de ciment selon la revendication 14, qui comprend 0,02 à 1,0 pour cent en poids basé sur le ciment, en termes de matière solide, du copolymère.
- 30 16. Utilisation du copolymère tel que défini selon l'une quelconque des revendications 1 à 10, pour mélanger et disperser un mélange de ciment.
- 35 17. Procédé de production du copolymère tel que défini selon l'une quelconque des revendications 1 à 10, par polymérisation des monomères (a) et (b) ou des monomères (a), (b) et (c) dans un solvant approprié à un rapport de réaction de 0,1 à 50 % en moles de (a) et 50 à 99,9 % en moles de (b), ou à un rapport de réaction de 0,1 à 50 % en moles de (a), 50 à 90 % en moles de (b), et 0,1 à 50 % en moles de (c).

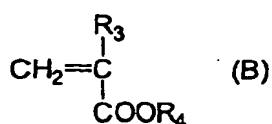
#### 40 Patentansprüche

1. Zementmischung, umfassend ein Copolymer, das im wesentlichen besteht aus: 0,1 bis 50 mol-% Einheiten, die von einem ethylenisch ungesättigten Monomer (a) mit 25 bis 300 mol  $C_{2-3}$ -Oxyalkylengruppen pro Molekül stammen, und 50 bis 99,9 mol-% Einheiten, die von einem Monomer (b) eines Alkyl-, Alkenyl- oder Hydroxyalkylesters einer ethylenisch ungesättigten Mono- oder Dicarbonsäure stammen, oder 0,1 bis 50 mol-% Einheiten, die von dem Monomer (a) stammen, 50 bis 90 mol-% Einheiten, die von dem Monomer (b) stammen, und 0,1 bis 50 mol-% Einheiten, die von einem Monomer (c) stammen, ausgewählt aus einer ethylenisch ungesättigten Monocarbonsäure, einem Salz davon, einer ethylenisch ungesättigten Dicarbonsäure und einem Anhydrid davon und einem Salz davon, als strukturelle Einheiten.
2. Mischung nach Anspruch 1, worin das Monomer (a) ausgewählt ist aus einem Esterprodukt von Methoxypolyalkylenglykol mit 25 bis 300 mol  $C_{2-3}$ -Oxyalkylengruppen pro Mol mit Acrylsäure oder Methacrylsäure, Monoallylether von Polyalkylenglykol mit 25 bis 300 mol  $C_{2-3}$ -Oxyalkylengruppen pro Mol und Maleinsäureanhydrid, Itaconsäureanhydrid, Citraconsäureanhydrid, Maleinsäure, Itaconsäure, Citraconsäure, Acrylamid und einem acrylischen Alkylamid, die jeweils 25 bis 300 mol an zugegebenen  $C_{2-3}$ -Oxyalkylengruppen pro Mol aufweisen.
3. Mischung nach Anspruch 1 oder 2, worin das Monomer (a) durch die Formel (A) definiert ist:



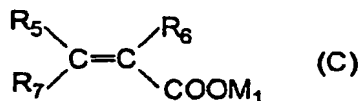
worin  $R_1$  und  $R_2$  jeweils ein Wasserstoffatom oder Methyl sind, AO eine  $C_{2-3}$ -Oxyalkylengruppe ist,  $n$  eine Zahl von 25 bis 300 ist und  $X$  ein Wasserstoffatom oder eine  $C_{1-3}$ -Alkylgruppe ist.

4. Zumischung nach Anspruch 3, worin  $n$  eine Zahl von 110 bis 300 ist.
5. Zumischung nach einem der Ansprüche 1 bis 4, worin das Monomer (b) ein ungesättigter Monocarboxylatester mit der Formel (B) ist:



worin  $R_3$  ein Wasserstoffatom oder Methyl ist und  $R_4$  eine  $C_{1-18}$ -Alkyl- oder -Alkenylgruppe oder eine  $C_{2-6}$ -Hydroxyalkylgruppe ist.

6. Zumischung nach einem der Ansprüche 1 bis 5, worin das Monomer (b) ausgewählt ist aus Äpfelsäurediester, Fumarsäurediester, Itaconsäurediester und Citraconsäurediester, wobei jeder Diester eine geradkettige oder verzweigte  $C_{1-18}$ -Alkyl- oder -Alkenylgruppe aufweist.
7. Zumischung nach einem der Ansprüche 1 bis 6, worin das Monomer (c) durch die Formel (C) definiert ist:



worin  $M_1$  ein Wasserstoffatom, Alkalimetall, Erdalkalimetall, Ammonium, Alkylammonium oder eine substituierte Alkylammoniumgruppe ist;  $R_5$ ,  $R_6$  und  $R_7$  jeweils ein Wasserstoffatom, Methyl oder  $(CH_2)_{m_2}COOM_2$  sind;  $M_2$  die gleiche Definition wie  $M_1$  aufweist;  $m_2$  0 oder 1 ist.

8. Zumischung nach einem der Ansprüche 1 bis 7, worin das Copolymer ein Molekulargewicht im Gewichtsmittel von 8.000 bis 1.000.000 hat.
9. Zumischung nach einem der Ansprüche 1 bis 8, worin das Copolymer 5 bis 40 mol-% der Einheiten (a), 50 bis 90 mol-% der Einheiten (b) und 5 bis 40 mol-% der Einheiten (c) umfasst.
10. Zumischung nach einem der Ansprüche 1 bis 9, worin das Copolymer 10 bis 30 mol-% der Einheiten (a), 50 bis 70 mol-% der Einheiten (b) und 10 bis 30 mol-% der Einheiten (c) umfasst.
11. Zementzumischungszusammensetzung, umfassend das Copolymer wie in einem der Ansprüche 1 bis 10 definiert und zumindest ein Hochleistungs-Wasser-Reduktionsmittel, ausgewählt aus der Gruppe, bestehend aus Naphthalinderivaten, Melaminderivaten, Aminsulfonsäurederivaten und Polycarbonsäurederivaten.

12. Zusammensetzung nach Anspruch 11, worin das Mischungsverhältnis des Copolymers zu dem Hochleistungs-Wasser-Reduktionsmittel im Bereich zwischen 10:90 und 90:10 liegt.

5 13. Verfahren zum Dispergieren einer Zementmischung mit dem Copolymer wie in einem der Ansprüche 1 bis 10 definiert.

14. Zementzusammensetzung, umfassend Zement, Aggregate und das Copolymer wie in einem der Ansprüche 1 bis 10 definiert.

10 15. Zementzusammensetzung nach Anspruch 14, umfassend 0,02 bis 1,0 Gew.% des Copolymers, bezogen auf den Zement und als Feststoff.

16. Verwendung des Copolymers wie in einem der Ansprüche 1 bis 10 definiert, zum Mischen und Dispergieren einer Zementmischung.

15 17. Verfahren zur Erzeugung des Copolymers wie in einem der Ansprüche 1 bis 10 definiert durch Polymerisieren der Monomere (a) und (b) oder der Monomere (a), (b) und (c) in einem geeigneten Lösungsmittel bei einem Reaktionsverhältnis von 0,1 bis 50 mol-% (a) und 50 bis 99,9 mol-% (b) oder bei einem Reaktionsverhältnis von 0,1 bis 50 mol-% (a), 50 bis 90 mol-% (b) und 0,1 bis 50 mol-% (c).